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**Final Report**  
**(11/1/2003 to 8/31/2004)**

**DEVELOPMENT OF A COMPREHENSIVE AND PREDICTIVE REACTION  
MECHANISM OF LIQUID HYDROCARBON FUEL COMBUSTION**

(Grant/Contract Number FA9550-04-1-0008)

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**SUMMARY/OVERVIEW:**

Studies were conducted to finalize a fundamental and predictive reaction model for the combustion of hydrogen and carbon monoxide through a multi-parameter optimization. These studies showed that reliable data of hydrogen and carbon monoxide oxidation at high temperatures can be reconciled by a single kinetic model. An advanced approach to solve the master equation of collision energy transfer was developed to predict the rate constants of combustion reactions of arbitrary complexities. Studies were also conducted on a class of unique combustion reactions that involve spin state crossing—one of the last few unresolved theoretical problems in combustion reaction kinetics.

**TECHNICAL DISCUSSION:**

**1. Optimization of H<sub>2</sub>/CO Combustion Chemistry**

In this collaborative project (with Professor Fokion Egolfopoulos of USC), we propose a H<sub>2</sub>-CO kinetic model which incorporates the recent thermodynamic, kinetic, and species transport updates relevant to high-temperature H<sub>2</sub> and CO oxidation [1]. Attention has been placed on obtaining a comprehensive and kinetically accurate model able to predict a wide variety of H<sub>2</sub>-CO combustion data. The model was subject to systematic optimization and validation tests against reliable H<sub>2</sub>-CO combustion data, from global combustion properties (shock-tube ignition delays, laminar flame speeds, and extinction strain rates) to detailed species profiles during H<sub>2</sub> and CO oxidation in flow-reactor and in laminar premixed flames. Although some of the features of model optimization have been reported in the last contractors meeting, the model presented herein represents our final effort in this area. Validation tests now include the extinction stretch rates of ultra-lean H<sub>2</sub>-air flames, not considered previously [2]. The optimized model will be used as a kinetic foundation for future studies of aliphatics combustion mechanisms.

The unoptimized (trial) reaction model consists of 14 species and 30 reactions. The trial model was based on a careful review of recent kinetics literature, considering both direct data and compilations. The diffusion coefficients of key pairs have been updated, as reported in the last year's annual report. These updates are reported in [2]. A comprehensive review was conducted for a large number of H<sub>2</sub>-CO combustion data. Thirty-six experiments were chosen as

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optimization targets. The targets can be classified into four categories: (1) laminar flame speeds of H<sub>2</sub>-air, H<sub>2</sub>-O<sub>2</sub>-He, and H<sub>2</sub>-CO-air mixtures, (2) the peak mole fractions of H and O in a low-pressure burner-stabilized H<sub>2</sub>-O<sub>2</sub>-Ar flame, (3) the consumption rates of H<sub>2</sub> and CO during the reaction of H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> and CO-O<sub>2</sub>-H<sub>2</sub>O-N<sub>2</sub> mixtures in a turbulent flow reactor, and (4) ignition delay times of H<sub>2</sub>-O<sub>2</sub>-Ar and H<sub>2</sub>-CO-O<sub>2</sub>-Ar mixtures behind reflected shock waves. Active parameters were identified through sensitivity analysis. The entire set of active parameters consists of 28 *A*-factors and third-body efficiency factors. Minimization was carried out on the objective function  $L^2 = \sum_i [(\eta_{i,\text{expt}} - \eta_{i,\text{calc}})/\sigma_i]^2$  subject to the constraints that the active parameters were bound by the ranges of their respective uncertainties. Each target was individually weighted by their uncertainty.

Selected validation results of the optimized model are briefly discussed here. Fig. 1 presents experimental and computed laminar flame speeds of H<sub>2</sub>-air and air-equivalent mixtures where N<sub>2</sub> was replaced by Ar or He. It is seen that the flame speeds predicted with the optimized model are in an excellent agreement with the experimental data. Figures 2 shows that the optimized model reproduces experimental H<sub>2</sub>-CO-air laminar flame speeds. Fig. 3 shows a plot of experimental and computed ignition delay times for H<sub>2</sub>-O<sub>2</sub>-Ar mixtures behind reflected shock waves. Here the experimental shock-tube ignition delay data were fitted into  $\tau (\mu\text{s}) = [\text{H}_2]^{-0.154} [\text{O}_2]^{0.693} [\text{Ar}]^{0.04} [6.77 \times 10^{-8} T^{0.252} e^{9234/T}]$  for non "run-away" data, i.e., those fall on the nearly linear portion of the curves of Fig. 3, where [] denotes concentration in mol/cm<sup>3</sup>. Figure 4 depicts species profiles for 4 selected H<sub>2</sub> oxidation experiments in a turbulent flow reactor. Similar results for moist CO oxidation are presented in Fig. 5, over an extended pressure range. The trial and optimized models were also tested against extinction strain rates of ultra-lean H<sub>2</sub>-air mixtures [2].

The optimization procedure also allows us to probe the residual kinetic uncertainties. For example, we found that the rate coefficient of H+O<sub>2</sub>=OH+O always stayed within 5% of the trial value for all optimization runs made, including the use of a smaller number of targets and/or a reduced dimensionality of active parameter space.

This work is reported in Refs. 1 and 2.

## 2. A Monte Carlo Master Equation Solver

The temperature and pressure dependence of the rate constants of chemically activated reactions is essential in combustion modeling. Many gas phase reactions proceed through the formation of ro-vibrationally excited adducts. The fate of the excited species is determined by several competing processes. Energy is transferred to and from the molecule as a consequence of inelastic collisions with the surrounding bath gas molecules. Between collisions, the molecule can undergo internal rearrangement or isomerization, decompose to form new products or simply dissociate back to the reactants. Much progress has been made in our understanding of collisional energy transfer and its influence on the temperature and pressure dependence of unimolecular and chemically activated reactions. Troe introduced a collision efficiency factor  $\beta_c$ , such that the rate constant at low pressure was related to the strong collision rate constant through  $k_0 \equiv \beta_c k_0^{sc}$ . The modified strong collision (MSC) approach thus allowed for weak collisions with the efficiency of energy transfer dependent on the nature of the bath gas. Though the modified strong collision model was intended for use only for single-channel unimolecular reactions, over the years this model has been widely used for multi-channel chemically activated reactions. The fundamental validity of this approach is certainly questionable. For this reason a Monte Carlo code was developed that can solve the master equation of collision energy transfer for unimolecular and chemically activated reactions of an arbitrary complexity. The code was fully validated and optimized. Comparisons with the MSC model were made. These comparisons show that the MSC model lead to large errors in rate constant calculations.

A second motivation for the development of the Monte Carlo code arises from our interest to tackle a fundamental kinetic problem not tackled previously, namely chemically activated reactions that involve spin-state crossing. A methodology is currently being developed and tested for these reactions, including those to be discussed in section 3.

This work is reported in Ref. 3.

### 3. Reactions on C<sub>2</sub>H<sub>4</sub>O and C<sub>6</sub>H<sub>6</sub>O Potential Energy Surfaces.

There are several motivations for this work. The reactions on the C<sub>2</sub>H<sub>4</sub>O and C<sub>6</sub>H<sub>6</sub>O potential energy surface involve multiple triplet and singlet spin-state crossings. These reactions are ideal for use as test cases of our Monte Carlo approach. The reactions on the C<sub>6</sub>H<sub>6</sub>O potential energy surface are critical to the fundamental kinetics of aromatics oxidation. The reaction model of aromatics is currently under development by our research group. The C<sub>2</sub>H<sub>4</sub>O reactions are important to an predictive ethylene oxide reaction model also under development. The latter effort was initiated following the request by the USAF Research Laboratory.

Quantum chemistry calculations at G3 and CASSCF levels of theory were carried out. The potential energy surfaces for both C<sub>2</sub>H<sub>4</sub>O and C<sub>6</sub>H<sub>6</sub>O are now complete, including all feasible spin-state crossing. Unique kinetic features resulting from spin-state crossing will be examined using the developed Monte Carlo code.

Parts of this work are reported in Ref. 4.

## **TECHNOLOGY TRANSFER**

The following technology transitions and transfers were made:

Performers: Dr. Hai Wang, University of Delaware, (302) 831-4464  
Dr. Fokion Egolfopoulos, University of Southern California, (213) 740-0480  
Customer: Dr. Bala Varatharajan, GE Global Research Center, One Research Circle,  
Building K-1, Room ES243, Niskayuna NY 12309.  
Phone: (518) 387-4133  
Result: Reaction model for hydrogen and propane combustion  
Application: NO<sub>x</sub> control in gas turbines

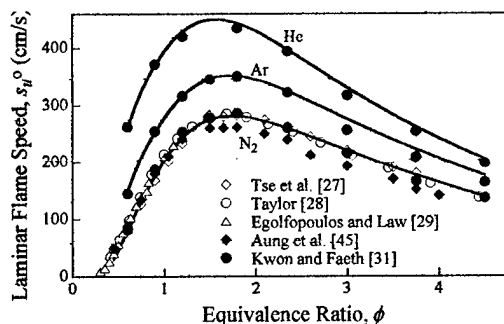
Performer: Dr. Hai Wang, University of Delaware, (302) 831-4464  
Customer: Dr. Biswadip Shome, GE Gas Turbines (Greenville) LLC, 300 Garlington Road,  
P.O. Box 648, Mail Sorter GTTL 1256, Greenville, SC 29602-0648.  
Phone: (864) 254-4623  
Result: Reaction model for hydrogen and carbon monoxide combustion  
Application: Flame holding in gas turbines

## **EXTRAMURAL-INTRAMURAL INTERACTIONS**

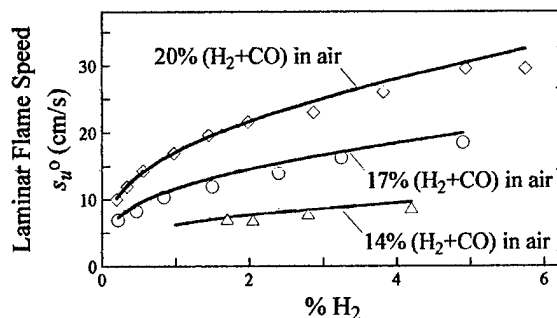
We worked closely with Dr. Dean Eklund and Dr. Thomas Jackson until their departure from the Wright-Patterson AFRL. Currently, our AFRL contact person is Dr. J. T Edwards. A visit to the Wright-Patterson AFRL has been scheduled for September 15, 2004. During the visit, the PI will meet and discuss potential research collaborations with various lab research personnel, and give a talk entitled "Incipient Soot Formation and Growth."

## AFOSR SPONSORED PUBLICATIONS AND PRESENTATIONS:

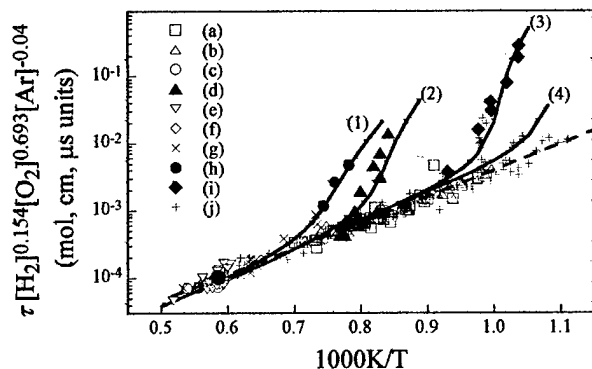
1. Davis, S. G., Joshi, A. V., Wang, H., and Egolfopoulos, F., "An optimized kinetic model of  $H_2/CO$  combustion," *Proceedings of the Combustion Institute*, accepted, 2003.
2. Dong, Y., Holley, A.T., Andac, M.G., Egolfopoulos, F.N. Davis, S. G., and Middha, P., Wang, H. "Experimental and Numerical Studies of Extinction of Premixed Lean  $H_2$ /Air Flames," 2004 Spring Technical Meeting of the Western States of the Combustion Institute, University of California at Davis, Davis, California, March, 2004, paper 04S-19 and submitted to *Combustion and Flame*, 2004.
3. Joshi, A. V., Wang, H., and Davis, S. G., "Multi-Channel Chemically Activated Reactions: Comparison of Troe's Weak Collision Model and Exact Solution of the Master Equation by Monte Carlo Method," 2004 Spring Technical Meeting of the Western States of the Combustion Institute, University of California at Davis, Davis, California, March 29&30, 2004, paper 04S-25.
4. Joshi, A. V., Davis, S. G., and Wang, H. "Ab-initio Study of the  $C_6H_5O + H$  Reaction: Viability of the  $CO + C_5H_6$  Channel," in *Chemical and Physical Processes in Combustion*, 2003 Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Pennsylvania State University, University Park, Pennsylvania, October 26-29, 2003.
5. Davis, S. G., Mhadeshwar, A. B., Vlachos, D. G., and Wang, H. "A new approach to response surface development for detailed gas-phase and surface reaction kinetic model development and optimization," *International Journal of Chemical Kinetics* 36: 94-106 (2003).
6. Law, C. K., Sung, C. J., Wang, H., and Lu, T. F. "Development of comprehensive detailed and reduced reaction mechanisms for combustion modeling," *AIAA Journal* 41: 1629-1646 (2003).



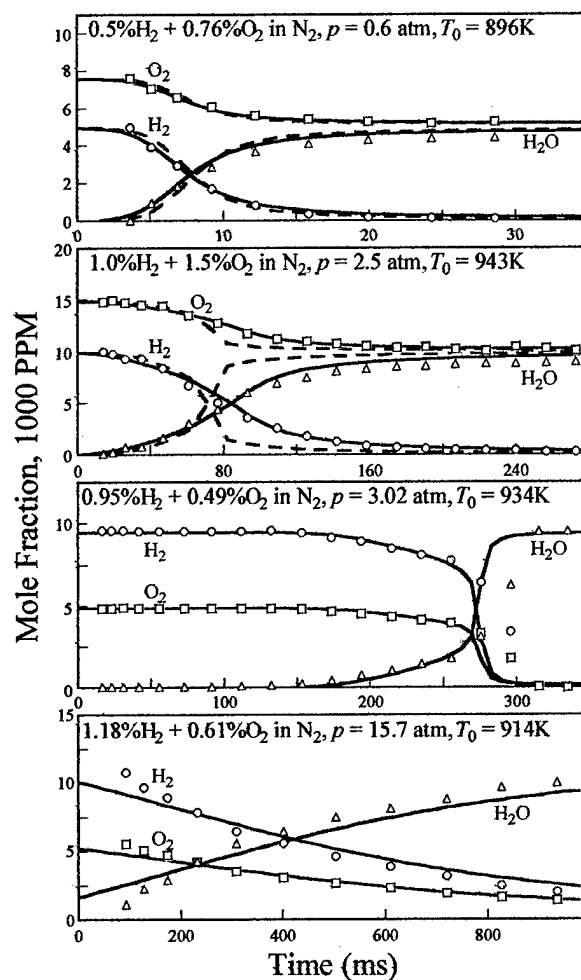
**Figure 1.** Experimental (symbols) [Tse, S. D., Zhu, D. L., and Law, C. K., *Proc. Combust. Inst.* 28, 1793-1800 (2000); Taylor, S. C., "Burning Velocity and the Influence of Flame Stretch," Ph.D. thesis, University of Leeds, 1991; Aung, K. T., Hassan, M. I., and Faeth, G. M., *Combust. Flame* 109, 1-24, (1997); Egolfopoulos, F. N. and Law, C. K., *Proc. Combust. Inst.* 23, 333-340 (1990); Kwon, O. C. and Faeth, G. M. *Combust. Flame* 124 590-610 (2001)] and computed (line) laminar flame speed of  $H_2$ -air and  $H_2$ -Ar- and He-substituted air mixtures at the atmospheric pressure.



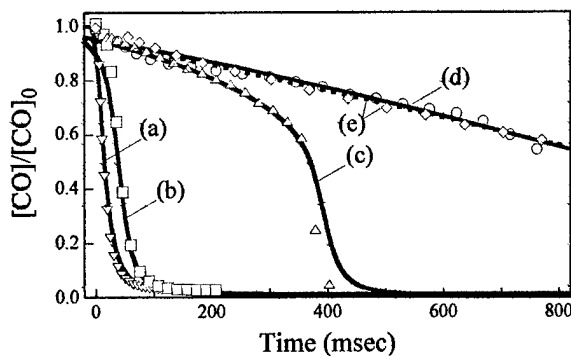
**Figure 2.** Experimental (symbols) [Vagelopoulos, C. M. and Egolfopoulos, F. N. *Proc. Combust. Inst.* 25, 1317-1323 (1994)] and computed (line) laminar flame speed of  $H_2$ -CO-air mixtures at the atmospheric pressure.



**Figure 3.** Experimental (symbols) and computed (lines) ignition delay times of  $H_2$ - $O_2$ -Ar mixtures behind reflected shock waves. Symbols: (a) 6.67%  $H_2$ +3.33%  $O_2$ ,  $p_5=1.35$ -2.90 atm; (b) 5%  $H_2$ +5%  $O_2$ ,  $p_5=1.35$ -2.90 atm (onset of pressure rise, [R. K. Cheng, A. K. Oppenheim, *Combust. Flame* 58, (1984) 125-139]), (c) 0.5%  $H_2$ +0.25%  $O_2$ ,  $p_5=33$  atm, (d) 2%  $H_2$ +1%  $O_2$ ,  $p_5=33$  atm, (e) 0.5%  $H_2$ +0.25%  $O_2$ ,  $p_5=57$  atm, (f) 0.33%  $H_2$ +0.17%  $O_2$ ,  $p_5=64$  atm, (g) 0.1%  $H_2$ +0.05%  $O_2$ ,  $p_5=64$  atm, (h) 0.5%  $H_2$ +0.25%  $O_2$ ,  $p_5=87$  atm (maximum OH absorption rate, [E. L. Peterson, D. F. Davidson, M. Rohrig, R. K. Hanson, 20<sup>th</sup> Int. Symp. on Shock Waves, 1996, pp. 941-946]), (i) 8%  $H_2$ +2%  $O_2$ ,  $p_5=5$  atm (maximum OH emission) [G. B. Skinner, G. H. Ringrose, *J. Chem. Phys.* 42 (1965) 2190-2192], (j) four  $H_2$ + $O_2$  mixtures [A. Cohen, J. Larsen, Report BRL 1386, 1967]. Lines: (1) 0.5%  $H_2$ +0.25%  $O_2$ ,  $p_5=87$  atm (maximum [OH] rate), (2) 2%  $H_2$ +1%  $O_2$ ,  $p_5=33$  atm (maximum [OH] rate), (3) 8%  $H_2$ +2%  $O_2$ ,  $p_5=5$  atm (maximum [OH]), (4) 5%  $H_2$ +5%  $O_2$ ,  $p_5=2$  atm (maximum pressure gradient).



**Figure 4.** Experimental (symbols) [Mueller, M. A., Kim, T. J., Yetter, R. A., and Dryer, F. L. *Int. J. Chem. Kinet.* 31, 113-125 (1999)] and computed (lines) species mole fraction profiles during hydrogen oxidation in a flow reactor. Solid lines: optimized model; dashed lines: trial model.



**Figure 5.** Experimental (symbols) [Kim, T. J., Yetter, R. A., Dryer, F. *Proc. Combust. Inst.* 25, 759-766 (1994)] and computed (lines)  $[CO]/[CO]_0$  profiles during moist CO oxidation in a flow reactor. Cases: (a) 1.014% CO+0.517%  $O_2$ +0.65%  $H_2O$  in  $N_2$ ,  $p=1$  atm,  $T_0=1038$  K, (b) 1.01% CO+0.496%  $O_2$ +0.65%  $H_2O$  in  $N_2$ ,  $p=2.44$  atm,  $T_0=1038$  K, (c) 0.988% CO+0.494%  $O_2$ +0.65%  $H_2O$  in  $N_2$ ,  $p=3.46$  atm,  $T_0=1038$  K, (d) 0.984% CO+0.497%  $O_2$ +0.65%  $H_2O$  in  $N_2$ ,  $p=6.5$  atm,  $T_0=1040$  K, (e) 0.994% CO+1.47%  $O_2$ +0.65%  $H_2O$  in  $N_2$ ,  $p=9.6$  atm,  $T_0=1039$  K.